

Chp L

LIMITED SMALL-SCALE FIELD STUDY FOR DESTRUCTION OF  
ORGANIC CONTAMINANTS BY ULTRAVIOLET/OZONE OXIDATION

INTERIM REPORT

by

D. W. Thompson, A. A. Khan, D. R. Puett,  
R. E. Bhuts, and N. R. Francingues

ENVIRONMENTAL EFFECTS LABORATORY  
U.S. ARMY ENGINEER WATERWAYS EXPERIMENT STATION  
P.O. BOX 631, VICKSBURG, MS. 39810

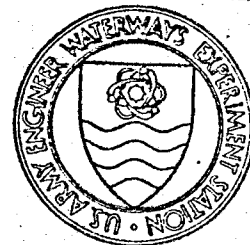
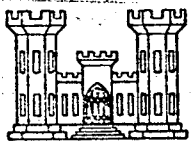
19941214 008

Prepared for: PROCESS DEVELOPMENT AND EVALUATION  
DIVISION ROCKY MOUNTAIN ARSENAL

DTIC QUALITY INSPECTED 1

Incl 1

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 10/01/77	3. REPORT TYPE AND DATES COVERED		
4. TITLE AND SUBTITLE LIMITED SMALL SCALE FIELD STUDY FOR DESTRUCTION OF ORGANIC CONTAMINANTS BY ULTRAVIOLET OZONE OXIDATION, INTERIM REPORT (DRAFT)		5. FUNDING NUMBERS		
6. AUTHOR(S) THOMPSON, D.; PUETT, D.; KHAN, A.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ARMY ENGINEER WATERWAYS EXPERIMENT STATION. ENVIRONMENTAL LABORATORY VICKSBURG, MS		8. PERFORMING ORGANIZATION REPORT NUMBER  81295R19		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) ROCKY MOUNTAIN ARSENAL (CO.) COMMERCE CITY, CO		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT  APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) THE PURPOSE OF THIS SMALL-SCALE FIELD STUDY WAS TO ASSESS THE POTENTIAL OF THE UV/OZONE PROCESS FOR REDUCING THE CONCENTRATION OF ORGANIC CONTAMINANTS IN RMA GROUND WATER IN A CONTINUOUS FLOW SYSTEM. THE SPECIFIC PURPOSE OF THIS REPORT IS TO PRESENT THE INTERIM RESULTS OF THE LIMITED SMALL-SCALE FIELD STUDY. A UV/OZONE ULTROX FIELD UNIT WA ACQUIRED AND SET UP IN BLDG. 802 AT RMA. THIS UNIT HAD A FLOW CAPACITY OF APPROXIMATELY 1000GPD. GROUND WATER WAS OBTAINED FROM A DESIGNATED WELL AND PUMPED THROUGH THE ULTROX UNIT. OPERATING PARAMETERS (OZONE) CONCENTRATION, LIQUID FLOW, UV INTENSITY, ETC.) WERE VARIED FOR EACH RUN ON THE BASIS OF INFORMATION OBTAINED FROM THE PREVIOUS RUNS WHICH HAD BEEN EVALUATED THROUGH THE USE OF A COMPUTER-AIDED ANALYSIS PROCEDURE. INFLUENT, MIDSTREAM AND EFFLUENT SAMPLES WERE COLLECTED AND ANALYZED. ALL AVAILABLE DATA WERE EVALUATED FOR USE IN THIS REPORT.				
14. SUBJECT TERMS ORGANIC ANALYSIS, METAL ANALYSIS, EQUIPMENT, DIMP, TOC			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT	



LIMITED SMALL-SCALE FIELD STUDY FOR DESTRUCTION OF  
ORGANIC CONTAMINANTS BY ULTRAVIOLET/OZONE OXIDATION

INTERIM REPORT

by

D. W. Thompson, A. A. Khan, D. R. Puett,  
R. E. Bhuts, and N. R. Francingues

ENVIRONMENTAL EFFECTS LABORATORY  
U.S. ARMY ENGINEER WATERWAYS EXPERIMENT STATION  
P.O. BOX 631, VICKSBURG, MS. 39810

Date: 1 October 1977

DRAFT

Accession For	
NTIS CRASH	<input checked="checked" type="checkbox"/>
ERIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Publication	
By	
Sponsor/	
Project/	
Task/	
Date/	
A-1	

Prepared for: PROCESS DEVELOPMENT AND EVALUATION  
DIVISION, ROCKY MOUNTAIN ARSENAL  
COMMERCE CITY, COLORADO 80022

## PREFACE

This investigation was conducted during the period 3 May 1977 to 30 September 1977 by the Environmental Effects Laboratory (EEL) of the U. S. Army Engineer Waterways Experiment Station (WES). The study was authorized by Intra-Army Order for Reimbursable Services No. RM 60-77, dated 3 May 1977, Rocky Mountain Arsenal, Commerce City, Colorado 80022.

This report was prepared by Douglas W. Thompson, LT Ashfaq A. Khan; CE, SP5 Danny R. Puett, CE, 1LT Robert E. Buhts, CE, and Norman R. Francingues of the Treatment Processes Research Branch, EEL, WES under the general supervision of Mr. Andrew J. Green, Chief, Environmental Engineering Division. Dr. John Harrison was Chief, EEL.

Special acknowledgment is extended to the following individuals for their assistance during the course of this work: Messrs. Carl Lovin, Ed Berry, Irwin Glassman, and Dr. Michael Witt (RMA); CPT Joe Kolmer and Mr. Dennis Wynne, Project Manager's Office for Installation Restoration; LTC Charles H. Coates, Ms. Nancy Weeks, Mr. Charles Ceasar, and Mr. Jack Dildine, (WES); also to the personnel of the Material Analysis Laboratory Group (RMA), the Analytical Laboratory Group (WES), and Messrs. Jack D. Zeff and Frank C. Farrell (Westgate Research Corporation).

COL J. L. Cannon, CE, was Commander and Director of the WES during the preparation of this report. Mr. F. R. Brown was Technical Director.

# CONTENTS

	Page
PREFACE . . . . .	1
LIST OF TABLES . . . . .	3
LIST OF FIGURES . . . . .	3
PART I: INTRODUCTION . . . . .	4
Background . . . . .	4
Purpose . . . . .	5
Scope . . . . .	5
Approach . . . . .	6
PART II: EQUIPMENT AND PROCEDURES . . . . .	7
Water Supply . . . . .	7
Ozone Generator . . . . .	7
ULTROX Treatment System . . . . .	9
Optimization Program . . . . .	11
Operational Procedures for the ULTROX System . . . . .	11
Sampling and Analysis . . . . .	12
PART III: RESULTS AND DISCUSSION . . . . .	14
Operational Parameters . . . . .	14
Organic Analysis . . . . .	16
Metals Analysis . . . . .	25
General Analysis . . . . .	26
Optimized Field Unit Operating Conditions . . . . .	26
PART IV: CONCLUSIONS AND RECOMMENDATIONS . . . . .	28
Conclusions . . . . .	28
Recommendations . . . . .	28
REFERENCES . . . . .	29
TABLES 1-6 . . . . .	30
APPENDIX A: OPERATING PROCEDURES FOR THE ULTROX SYSTEM . . . . .	38
APPENDIX B: OZONE SAMPLING AND ANALYSIS PROCEDURES . . . . .	40
APPENDIX C: DETERMINATION OF OPERATIONAL PARAMETERS FOR THE ULTROX SYSTEM . . . . .	43
APPENDIX D: GENERAL ANALYSIS FROM VARIOUS UV/OZONE TEST RUNS . . . .	46

## LIST OF TABLES

<u>No.</u>		Page
1	General Analysis Conducted on RMA Groundwater .....	30
2	Operational Parameters for Various UV/Ozone Test Runs ...	31
3	Organic Analysis for Various UV/Ozone Test Runs .....	33
4	Summary of Analysis - Metals .....	35
5	Summary of Analysis - General .....	36
6	Optimized Field Unit Operating Conditions .....	37

## LIST OF FIGURES

1	ULTROX Unit Set-Up at RMA .....	8
2	Diagram of ULTROX Reactor Chamber .....	10
3	Influent Flow vs Retention Time .....	15
4	DIMP Disappearance vs Ozone Mass Flow .....	18
5	DIMP Disappearance vs Number of UV Lamps .....	19
6	DIMP Disappearance vs Ozone Mass Flow with Fixed Oxygen Flow .....	20
7	DIMP Disappearance vs Liquid Feed Flow .....	21
8	TOC Reduction vs Ozone Mass Flow .....	23
9	TOC Reduction vs Number of UV/Lamps .....	24

LIMITED SMALL-SCALE FIELD STUDY  
FOR DESTRUCTION OF ORGANIC CONTAMINANTS  
BY ULTRAVIOLET/OZONE OXIDATION

PART I: INTRODUCTION

Background

1. Rocky Mountain Arsenal (RMA) has been a chemical manufacturing and ordnance demilitarization facility for the past 34 years. Military operations at the facility have included the production of chemical agents, the fabrication of munitions containing these agents, and the demilitarization of such munitions. Private corporations, under a lease agreement with the Army, have used certain industrial facilities at RMA for the production of pesticides. While most of the military operations have been concluded, a private company is still using certain facilities for pesticide production.

2. Waste products resulting from activities at RMA have been discharged into basins or otherwise disposed of within the boundaries of the arsenal. An extensive analysis program at RMA has indicated that some of the waste products have migrated from disposal sites to the groundwater.<sup>1</sup> Both organic and inorganic contaminants in varying amounts have been found in the groundwater.

3. The Colorado State Health Department (CSHD) informed RMA in April 1975 that diisopropylmethylphosphonate (DIMP) and dicyclopentadiene (DCPD) had been identified in an aquifer north of RMA. The CSHD requested (in the form of a cease and desist order) that efforts be made to remove these contaminants from the groundwater flowing across the arsenal boundary. Work was initiated in September 1975 to determine the applicability of selected treatment processes in removing DIMP and DCPD from the groundwater.<sup>2</sup> Two processes were found to be particularly effective in reducing DIMP and DCPD concentrations in water during preliminary testing. These processes are carbon adsorption and ozone

oxidation. Additional literature review<sup>3</sup> indicated that ultraviolet radiation would increase the effectiveness of ozone oxidation. Bench studies conducted on RMA groundwater using the two processes verified the results of the earlier tests.<sup>3,4</sup>

4. The bench-scale UV/ozone study report recommended that a small-scale field unit be obtained and installed at RMA.<sup>3</sup> The field unit was to be used to assess the treatability of groundwater obtained from several different sampling locations at RMA.

#### Purpose

5. The purpose of this small-scale field study was to assess the potential of the UV/ozone process for reducing the concentration of organic contaminants in RMA groundwater in a continuous flow system. Additional objectives of this study were as follows:

- a. To determine the relationship between operating conditions for the UV/ozone system and disappearance of organic contaminants in the treated groundwater.
- b. To determine modifications in procedures or design of the UV/ozone system that should be evaluated.
- c. To obtain the necessary information for design of a full size pilot plant including estimated operating and maintenance costs.

The specific purpose of this report is to present the interim results of the limited small-scale field study.

#### Scope

6. This report describes the work completed on a limited small-scale field study aimed at evaluating a field scale UV/ozone treatment system for reducing organic contaminant concentrations in RMA groundwater. All data available at the present time have been included in this report. These data have been evaluated to determine the relationship between operational parameters and the disappearance of organic contaminants in the sample waters and to provide estimated costs for a full-size treatment system. Work is still being conducted at RMA by

WES personnel with the UV/ozone unit and data obtained will be reported and evaluated in the final report.

### Approach

7. An UV/ozone ULTROX\* field unit was acquired and set up in Building 802 at RMA. This unit had a flow capacity of approximately 1000 gpd. Groundwater was obtained from a designated well and pumped through the ULTROX unit. Operating parameters (ozone concentration, liquid flow, UV intensity, etc.) were varied for each run on the basis of information obtained from the previous runs which had been evaluated through the use of a computer-aided analysis procedure. Influent, midstream, and effluent samples were collected and analyzed. All available data were evaluated for use in preparing this report.

---

\* ULTROX is a trade name for a unit manufactured by WESTGATE RESEARCH CORP, Los Angeles, California.

## PART II: EQUIPMENT AND PROCEDURES

### Water Supply

8. The groundwater used in the study was obtained from a well designated Pump Well 3 (PW3). Identical pumping procedures were used each time that water was taken from the well. The water quality remained fairly constant throughout the study.

9. The water was transported from PW3 to a covered storage tank near Building 802 in which the ULTROX unit was located. The storage tank and cover were constructed of rubber. The tank had a volume of approximately 3000 gallons.

10. The water was pumped out of the tank, into the project building, through a sand filter, and into the ULTROX unit. The sand filter was used to remove any grit or sand that might plug the flowmeters or otherwise damage the ULTROX unit. Samples of water were taken before and after the sand filter and analyzed. No significant differences in composition were found.

### Ozone Generator

11. Ozone was produced with an OREC, model 03B20 ozone generator (Figure 1). Its rated capacity was two pounds of ozone per day with oxygen feed. The concentration of ozone produced in the oxygen-ozone mixture could be varied over a range of 0.5 to 4 percent by weight by varying the ratio of power input to oxygen flow. Oxygen was supplied from a set of three standard gas cylinders connected by a manifold to the ozone generator.

12. The concentration of ozone in the oxygen-ozone mixture was determined by an iodometric titration that is discussed later in this report. The oxygen-ozone mixture passed from the ozone generator to the ULTROX unit through a parallel set of three needle valves followed in series by three flowmeters. This arrangement allowed for the

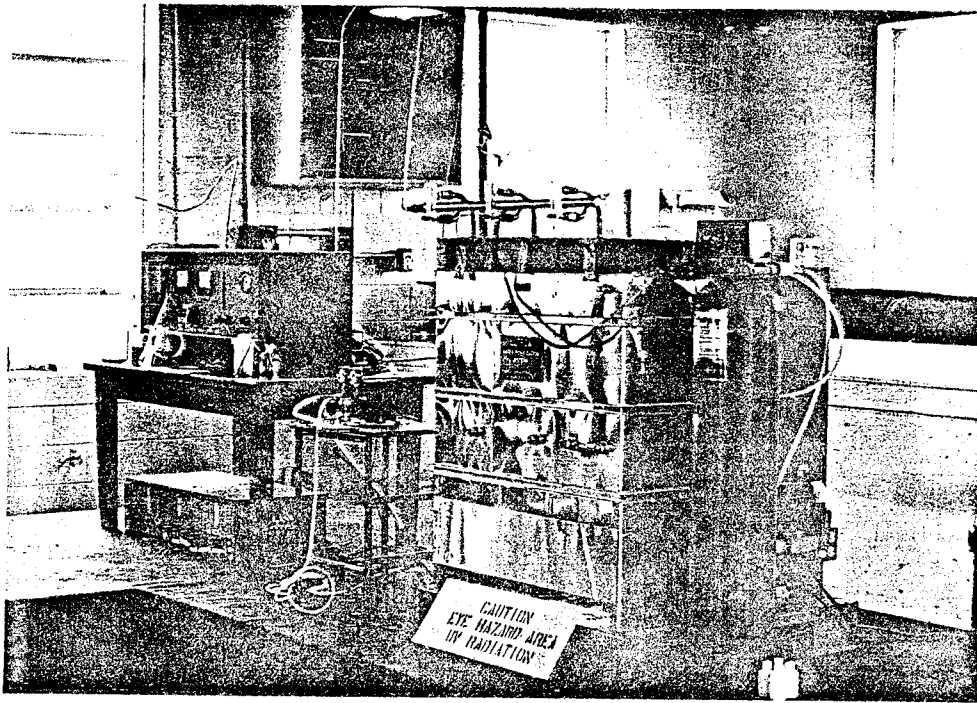


Figure 1. ULTROX unit Set-Up at RMA

introduction of different amounts of ozone to different stages in the ULTROX unit.

#### ULTROX Treatment System

13. The ULTROX unit is small-scale continuous flow UV/ozone treatment test system designed to be transported to a treatment site and operated on a side-stream of the contaminated water (Figure 1). The following operational parameters could be varied in the unit: (a) UV light, input and intensity, (b) ozone, introduction and concentration, and (c) water flow rate. The UV/ozone reactor chamber of the ULTROX unit is shown in Figure 2. The reactor width, length, and height dimensions are 18, 36, and 28 inches, respectively. The capacity of the unit was approximately 300 liters. The unit was rated for a flow rate of 1000 gpd. The reactor vessel was made of 304 stainless steel that had been passivated and electropolished to reduce chemical attack and increase UV reflectivity.

14. The reactor chamber was divided into six stages by baffles that provide a tortuous path for liquid flow through the chamber. Each stage contained eight porous ceramic spheres near the bottom of the chamber through which the oxygen-ozone mixture was sparged. All 48 spargers were used during the testing program. The spargers were capable of generating gas bubbles of less than 2.5 mm in diameter. Ultra-violet light was introduced by means of five quartz-jacketed ultraviolet lamps placed in each stage providing for a total of 30 lamps. (For the RMA study, 29 lamps of 40 watts each were used thus leaving a port for the introduction into the reactor of a midstream sampling tube.) These lamps were individually controlled thus permitting the regulation of UV intensity.

15. As mentioned in paragraph 12, the oxygen-ozone mixture entered the ULTROX unit through three parallel needle valve-flowmeter combinations. Each regulator controlled the flow of the gas mixture to two stages thus allowing different parts of the reactor to receive different flowrates of gas.

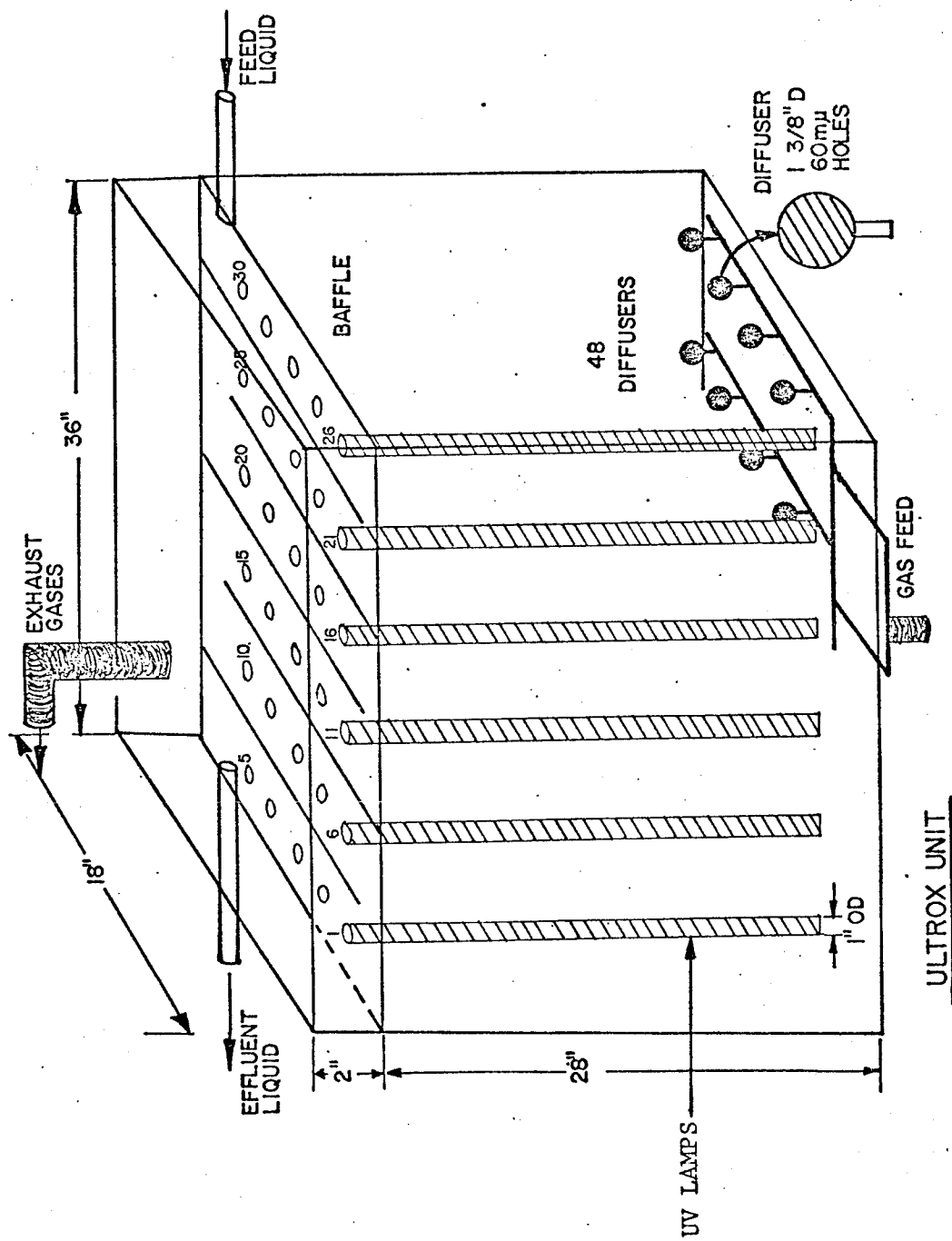


Figure 2. Diagram of ULTROX reactor chamber

16. The effluent from the reactor vessel passed through a liquid-gas separator to remove any residual ozone from the liquid. The liquid was discharged from the separator while the gas was combined with the exhaust gas from the reactor vessel. All waste gas then passed through a high temperature-catalytic system where any residual ozone or organic gases were decomposed before being vented to the atmosphere. The exhaust gas sampling port was located in such a manner as to provide for sampling before the gas passed through the high temperature-catalytic converter.

#### Optimization Program

17. Initial operating parameters for the ULTROX unit were determined by extrapolation of data from earlier bench test work. After the initial run, a computer-aided analysis procedure was used to determine the operating parameters for the next run.

18. The analysis procedure used a computer program that was leased along with the ULTROX unit. The computer program required an input consisting of the test conditions (i.e., liquid and gas flow rates, effluent analysis, pH, temperature, etc.) and it output a statistically determined set of new operating parameters.

19. In the RMA study, test conditions for each run were input to the program at the conclusion of each run. The program then provided the operating parameters to be used for the following run. At the conclusion of the test program, the computer program was used to develop recommended operating parameters for the ULTROX system to produce an effluent of specified quality. All work was conducted with regard to disappearance of DIMP because DCPD levels were below detectable limits in groundwater samples.

#### Operational Procedures for the ULTROX System

20. A set of operational procedures was established for the ULTROX system to insure reproducibility of results from the test program.

The operational parameters that were adjusted and evaluated included the liquid flow rate, ozone mass flow, ozone concentration, and lamp configuration. The start-up and shut-down procedures for the ULTROX system are described in Appendix A. The sampling procedures used to check the various operational parameters are discussed in other sections of this report.

21. After start-up, the ULTROX unit was operated and Total Organic Carbon (TOC) measurements made until it was determined that the system had reached "steady-state conditions", (i.e. until the effluent TOC values remained constant). Operating parameters were checked constantly throughout the run. Each run took about five hours to complete.

### Sampling and Analysis

#### Sampling

22. Most samples were taken near the end of the experimental run to insure that "steady-state" conditions had been reached. Ozone concentration in the gas flow to the ULTROX unit was measured periodically throughout the run. Grab samples were obtained from the influent stream, from a midstream sampling port, and from the effluent stream. Ozone sampling required a special procedure (see Appendix B).

23. Samples for dissolved oxygen measurement and organic analysis were collected in glass sample bottles. Dissolved oxygen measurements were made immediately after sample collection. Samples collected for Chemical Oxygen Demand (COD) analysis were preserved with concentrated  $H_2SO_4$ . Samples collected for TOC analysis were preserved with concentrated HCL.

24. Samples for metal analysis were collected in 125-ml plastic bottles and preserved with concentrated  $HNO_3$ . Samples for other tests were collected in 500-ml plastic bottles for immediate analysis.

#### Analysis

25. All analyses were performed as soon as possible. When delays were necessary, the samples were preserved as outlined in Standard Methods.

26.. Organic Analysis. Organic analyses for DIMP, DCPD, pesticides, and organo-sulfur compounds were conducted at RMA by MALD using gas chromatographic techniques. COD analyses were conducted onsite by WES personnel using the procedure given in Standard Methods for low level determinations. TOC analyses were conducted onsite and then the samples were shipped to WES for verification. All TOC analyses were conducted using the procedure given in Standard Methods.

27. Ozone Analysis. Ozone analyses were performed onsite using a iodometric titration technique as described in the operating manual for the OREC Model 03B20 ozone generator. This procedure is based on the iodometric titration procedure given in Standard Methods. An outline of the procedure used is presented in Appendix B of this report.

28. Metals Analysis. Samples collected for metals analyses were preserved and transported to WES. A scan was conducted on the samples using a Spectrametrics multi-element argon plasma spectrometer. Trace metal work was conducted on a Perkin-Elmer 503 atomic adsorption spectrophotometer. The unit was equipped with a heated graphite atomizer (HGA).

29. General Analysis. Other analyses that were performed are shown in Table 1. All testing was conducted on site except for solids analysis which was done at WES. Conductivity and pH analyses were conducted according to the manufacturers' operating manual. The remaining analyses were conducted according to procedures presented in Standard Methods or in Procedures for Water and Wastewater Analysis.<sup>6</sup> This latter publication presents procedures as adopted for use with a Bausch and Lomb Model 20 spectrophotometer.

### PART III: RESULTS AND DISCUSSION

#### Operational Parameters

30. The operational parameters for the various UV/ozone test runs conducted at RMA are presented in Table 2. As indicated, a total of 49 test runs were made. The first 35 runs were included in the optimization program. The operational parameter values were selected by use of computer-aided analysis. The last 14 runs were extra runs conducted to obtain data for a mathematical model being developed by WES. This model will be included in the final report. The parameter values were selected by the model developers.

##### Influent flow

31. The influent flow was varied from a low of 1 l/min to a high of 4 l/min. The retention times for the ULTROX unit corresponding to the influent flowrates are given in Figure 3.

##### Number of lamps

32. A total of 29 lamps were available for use in the ULTROX unit. The number used varied from none to all 29. This system allowed varying intensities of UV light to be introduced in different stages of the reaction chamber. The numbering system for the lamps is shown in Figure 2.

##### Ozone

33. Input. The ozone mass flow into the ULTROX unit was varied from 0 to 700 mg/min. In Runs 27 through 35 the ozone mass flow was distributed unequally into different parts of the reactor chamber as indicated in Table 2. For all other runs, the ozone mass flow was distributed equally through the chamber.

34. Exhaust gas. The ozone mass flow in the exhaust gas varied from 0 to 173 mg/min. The highest ozone mass flow out of the ULTROX unit occurred when all of the lamps were off during the run.

35. Dissolved in effluent. The ozone mass flow associated with the effluent stream was generally low (0 - 20 mg/min). Residual ozone decomposes rapidly and therefore poses no problems in the disposal of the effluent.

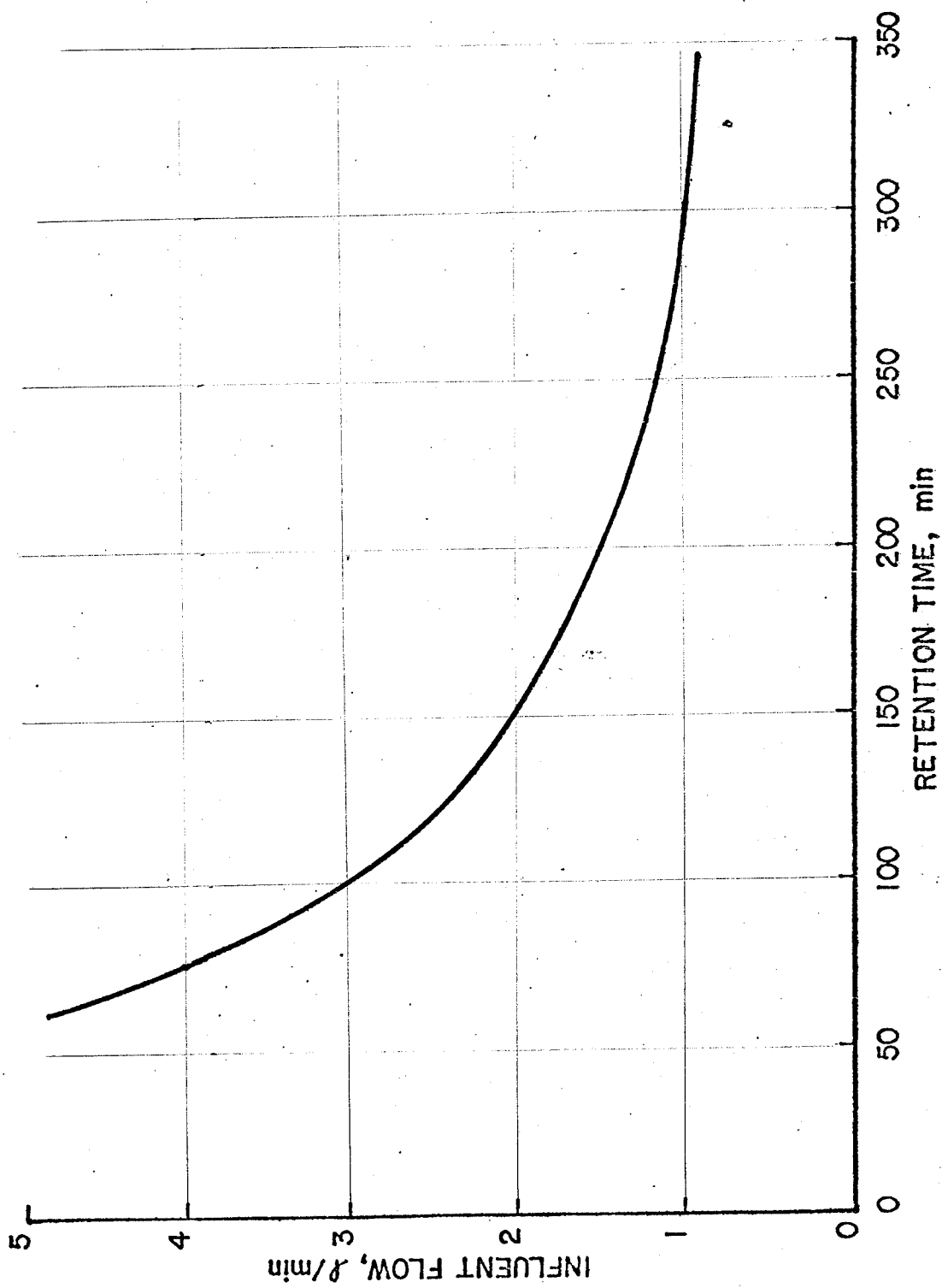


Figure 3. Influent flow vs retention time

### Oxygen

36. Gas flow. Oxygen flow into the system varied from 0 to 28 l/min. The variation in gas flow to the system can result in different mixing characteristics inside the reactor chamber.

37. Dissolved. The great variation in the dissolved oxygen concentration between the influent (approx 6 - 8 mg/l) and effluent (approx 35 - 45 mg/l) was a result of the high concentration of oxygen passed through the system. The dissolved oxygen concentration rapidly decreased when the effluent was allowed to come into contact with the atmosphere.

### Organic Analysis

38. The results of organic analyses conducted on samples from the various test runs are presented in Table 3. DIMP analysis was conducted on samples from all the runs. TOC and COD analyses were performed on most of the samples from the first 35 runs. DCPD, pesticide, and organo-sulfur analyses indicated influent concentrations at or below the detection limit of the equipment used. Therefore, these analyses were discontinued.

### DIMP

39. The average DIMP concentration in the influent was approximately 3000 ppb. The DIMP concentrations in the midstream and effluent samples varied greatly depending on the operational parameter settings used in a particular run. The lowest DIMP concentrations in the midstream and effluent samples were approximately 27 ppb and 3 ppb respectively. These samples were taken during Run 64 where an extremely long retention time (300 min) was used. The lowest percent DIMP disappearance occurred in Runs 94 and 95 where only UV radiation (no ozone) was used.

40. In order to illustrate the relationships between the operational parameters and DIMP disappearance, a series of graphs were developed and are presented as Figures 4-7. The operational parameter values are plotted against percent DIMP disappearance. Midstream and effluent values are represented by empty and solid symbols, respectively.

41. Ozone mass flow. Figure 4 illustrates the relationship between DIMP disappearance and ozone mass flow. DIMP disappearance increased rapidly until the ozone mass flow rate reached 300 mg/min. Then the percent DIMP disappearance increased only slightly except in the runs made with no UV radiation. In this case, the increase in ozone mass flow resulted in a substantial increase in DIMP disappearance. This plot also indicates the importance of UV radiation in reducing DIMP concentrations in the effluent.

42. Number of UV lamps. Figure 5 further illustrates the relationship between DIMP disappearance and the number of operating UV lamps. The percent DIMP disappearance increased rapidly until the number of lamps in operation reached 10. The use of additional lamps affected the percent DIMP disappearance only slightly.

43. Ozone mass flow with fixed oxygen flow. Figure 6 illustrates the relationship between DIMP disappearance and ozone mass flow with a constant oxygen flow. This plot again indicates that DIMP disappearance increased rapidly with respect to ozone mass flow up to a flow rate of 300 mg/min. The plot also indicates that the percent DIMP disappearance was higher at the higher oxygen flow rate (20 l/min) for the lower end of the ozone mass flow scale. This was attributed to increased mixing action as a result of a higher gas flow through the reactor.

44. Liquid feed flow. Figure 7 illustrates the relationship between DIMP disappearance and liquid feed (influent) flow. The percent DIMP disappearance decreased only slightly as the influent flow was increased to 4 l/min. As shown in Figure 3, an influent flow of 4 l/min corresponded to a retention time of 75 minutes. The midstream samples results can be used to approximate results that would be obtained from test runs made using influent flows twice as high as those actually used. Figure 7 indicates that percent DIMP disappearance would decrease more rapidly as the liquid feed flow increases above 4 l/min.

#### TOC

45. The average TOC concentration in the influent was 8.6 mg/l. The TOC concentrations in the midstream and effluent samples varied



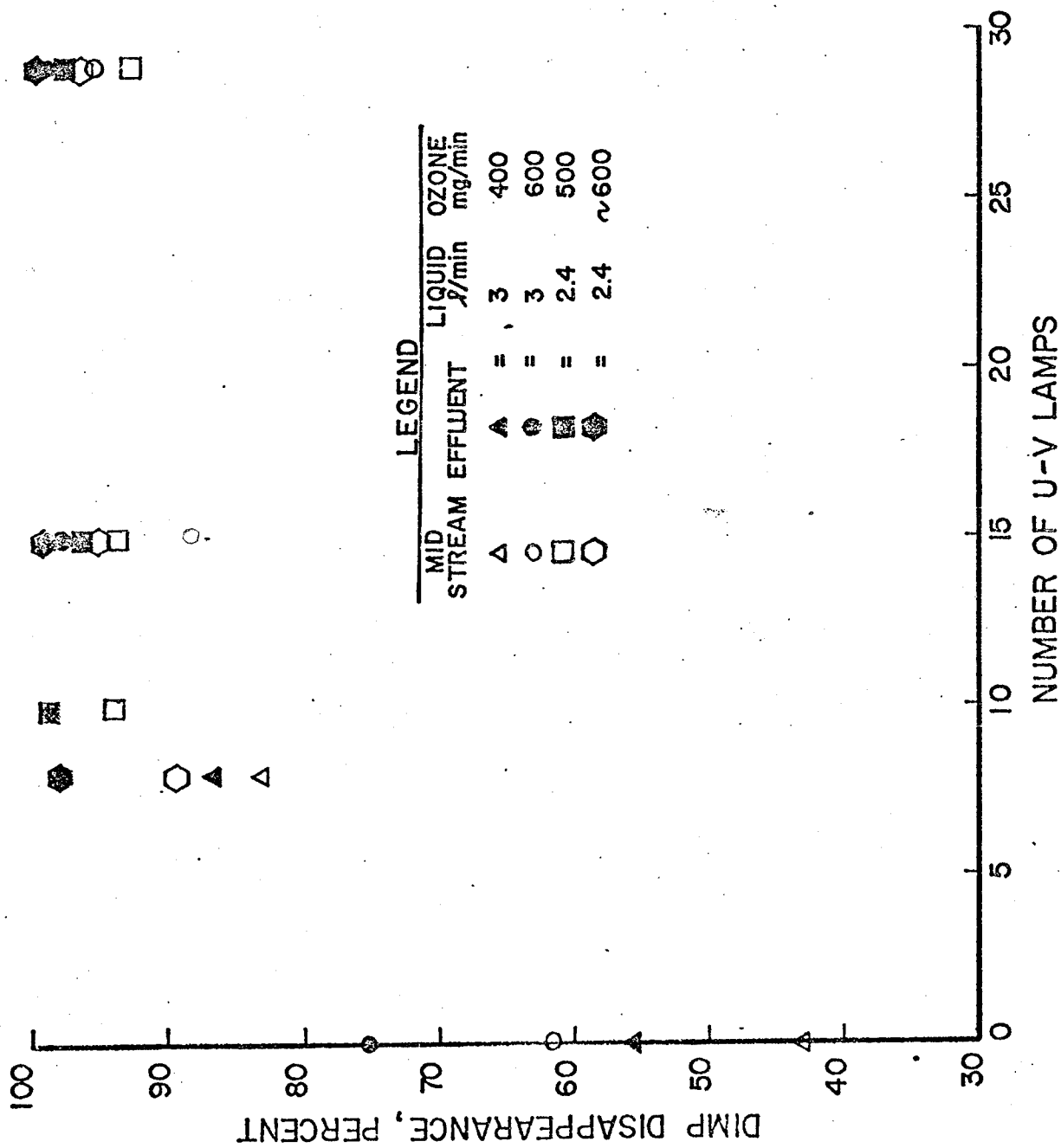


Figure 5. DIMP disappearance vs number of UV lamps

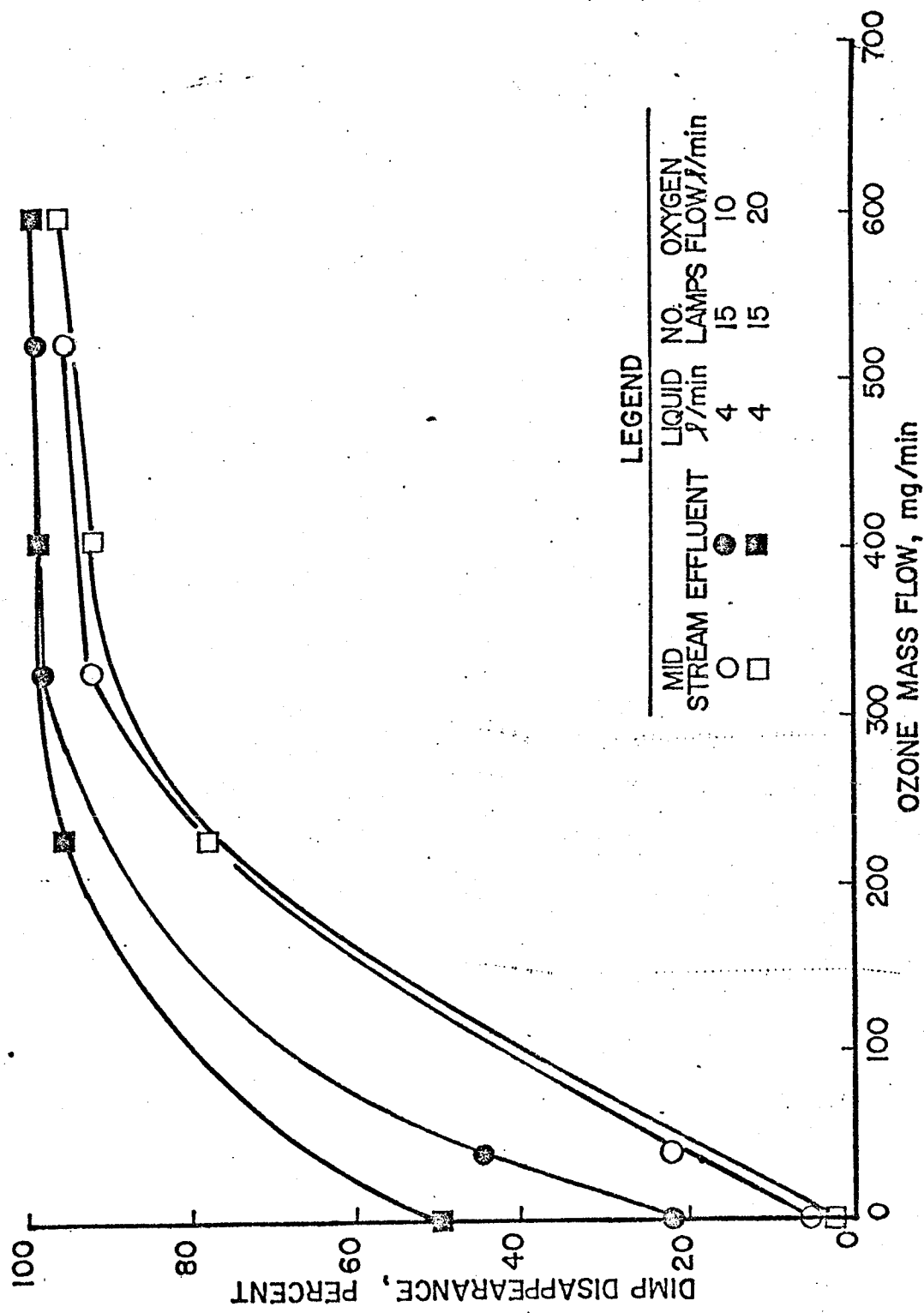


Figure 6. DIMP disappearance vs ozone mass flow with fixed oxygen flow

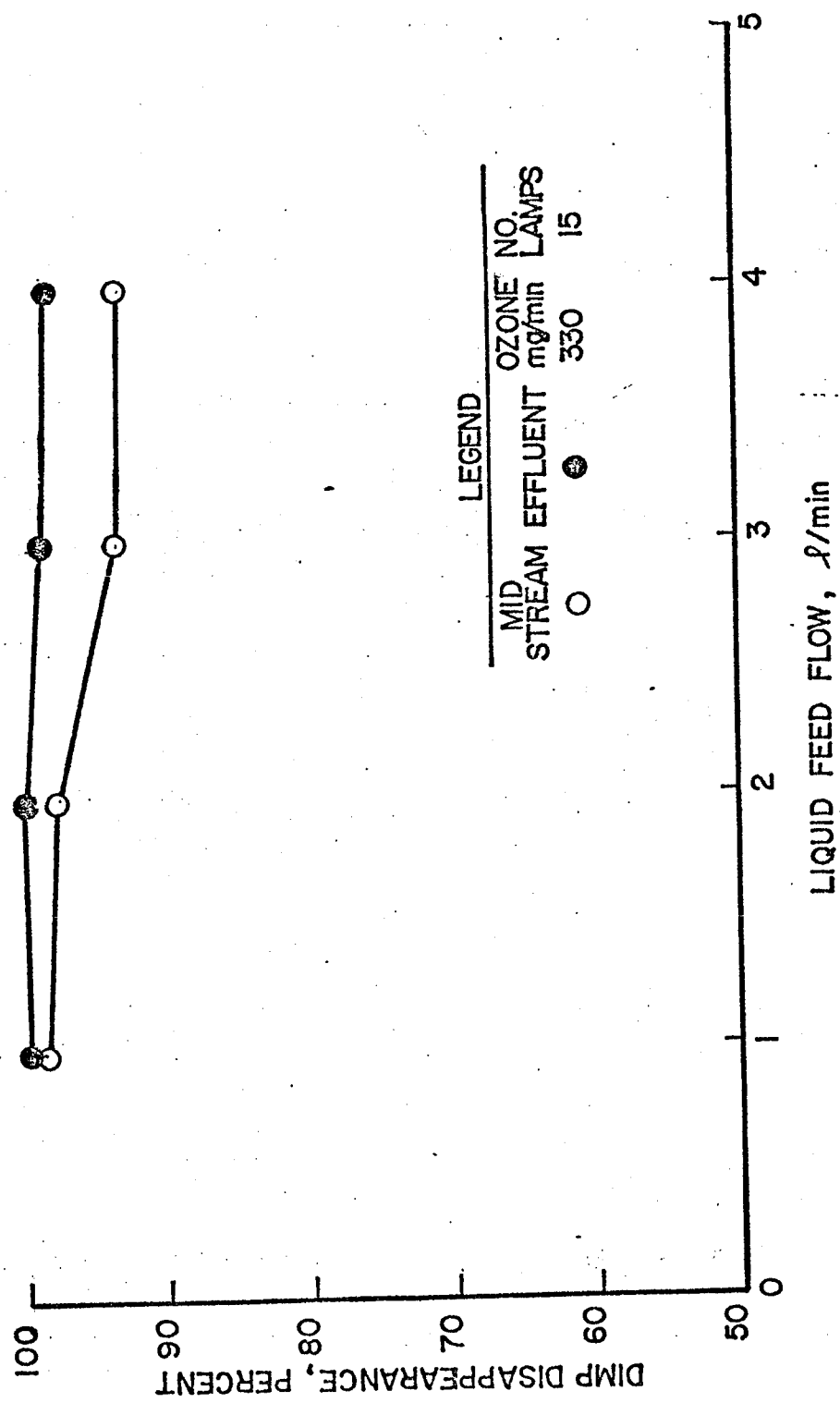


Figure 7. DIMP disappearance vs liquid feed flow

greatly in a range from 2 to 7 mg/l (Table 3). The percent reduction in TOC in the various samples appeared to follow the percent disappearance of DIMP but to a lesser degree.

46. The use of reduction in TOC concentration as a measure of the success of a treatment process can be misleading. This is particularly true in the case of the groundwater used in this study. A reduction in TOC indicates that organic molecules have been broken down to  $\text{CO}_2$  and other products. However, only those carbon atoms removed from an organic molecule and oxidized to  $\text{CO}_2$  show up as a decrease in TOC. For example, an organic molecule could be reduced to several shorter chain organic molecules by an oxidation reaction. The resulting organic molecules would manifest themselves as TOC although the original molecule was destroyed. This result occurs in the case of DIMP, which is the reason DIMP disappearance provides a better measure than TOC with regard to the effectiveness of UVO process.

47. The DIMP concentration in the influent averaged only 3 ppm. Even the complete destruction of all the DIMP would not account for the indicated reduction in TOC. Therefore, other trace organics were being destroyed as a result of the UV/ozone oxidation. The TOC remaining in the effluent stream, although not excessive in most cases, indicated that some decomposition organics were not being destroyed by the UV/ozone process.

48. In order to illustrate the relationships between the operational parameters of the ULTROX unit and TOC reduction, two graphs were developed and are presented as Figures 8-9. The operational parameter values are plotted against percent TOC reduction. Midstream and effluent values are represented by empty and solid symbols respectively. A discussion of the operational parameters follows.

49. Ozone mass flow. Figure 8 illustrates the relationship between TOC reduction and ozone mass flow. Unlike DIMP disappearance, TOC reduction increased significantly with increasing ozone mass flow even at flow rates of 600 mg/min. This plot also shows that TOC reduction increased significantly with increasing numbers of UV lamps.

50. Number of UV lamps. Figure 9 further illustrates the relationship between TOC reduction and the number of UV lamps. TOC reduction

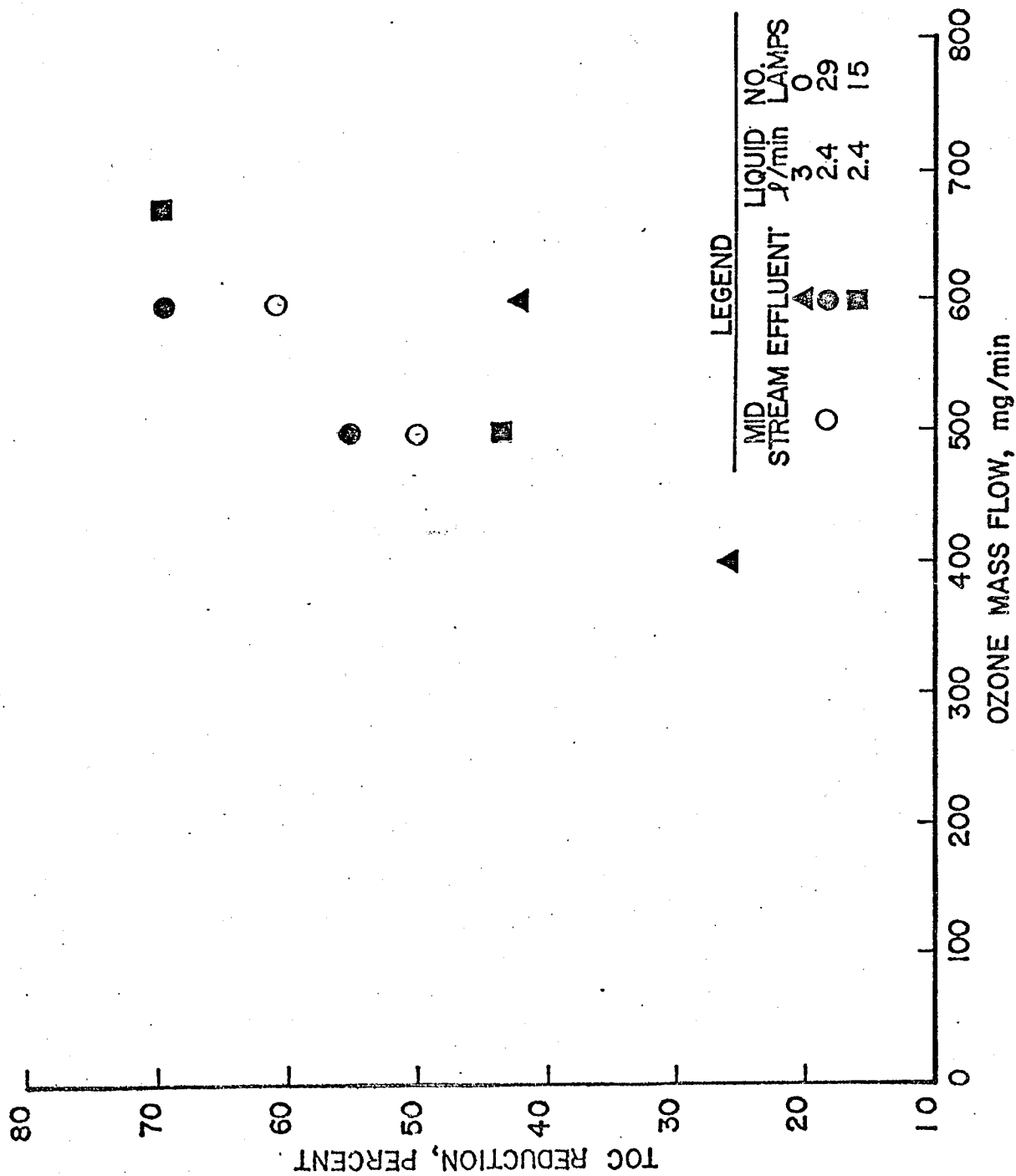


Figure 8. TOC reduction vs ozone mass flow

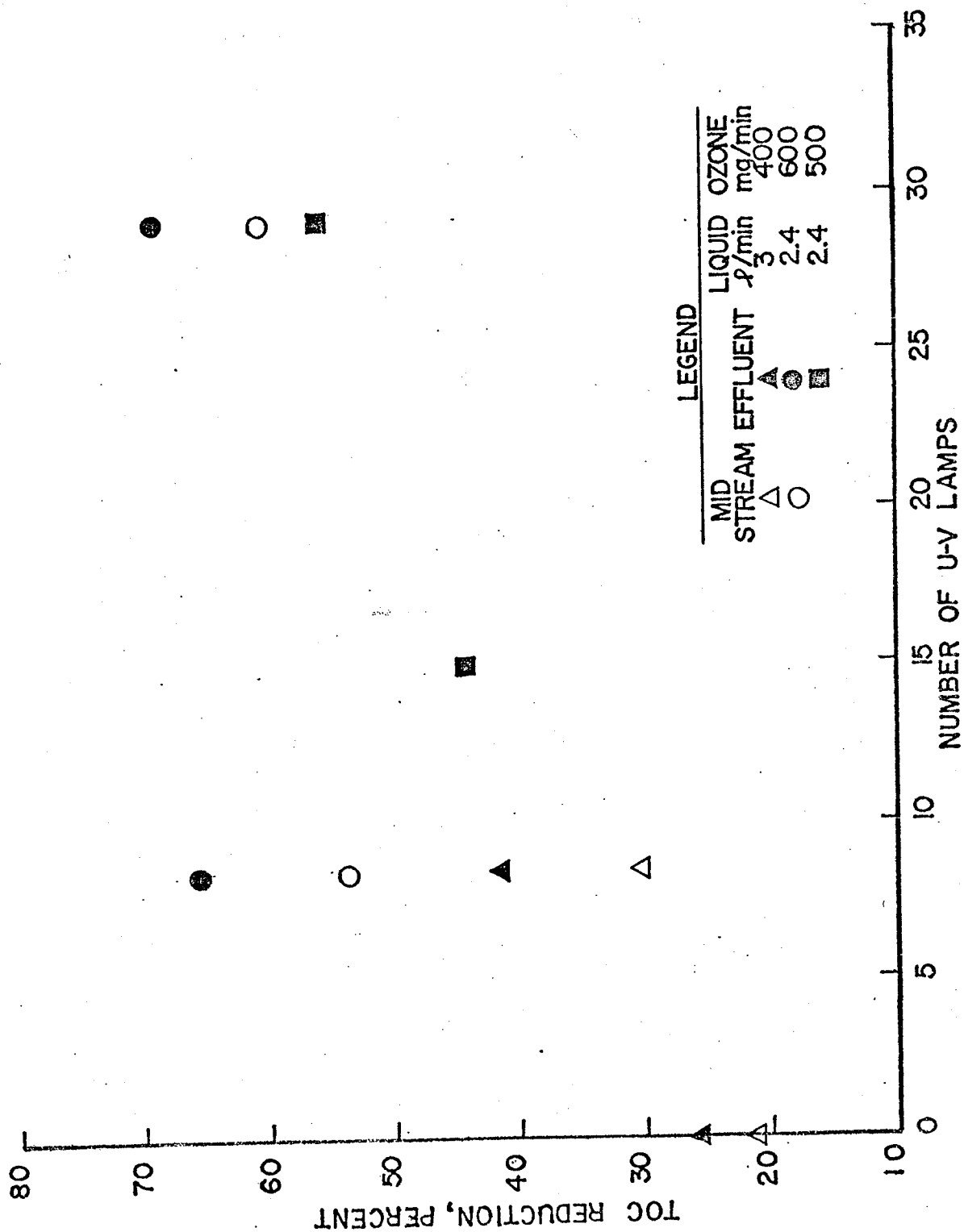


Figure 9. TOC reduction vs number of UV lamps

increased significantly, as compared to DIMP disappearance, as the number of lamps in operation increased. The increase in TOC reduction with increasing number of lamps was not as great at high ozone mass flows.

51. In comparing the TOC reduction plots to the DIMP disappearance plots, it appears that much higher ozone mass flow rates and UV intensity were needed to effect a high TOC reduction than were needed to effect fairly complete disappearance of DIMP.

#### COD

52. The average COD of the influent stream was approximately 19 mg/l. The COD of the effluent varied from 1.6 to 14.6 mg/l depending on the run. The COD data provided another check on the amount of decomposition of organic material contained in the effluent from the ULTROX unit. The data verified that certain organic contaminants had not been destroyed by the UV/ozone oxidation process.

#### Additional analysis

53. In order to identify the decomposition organics in the effluent from the ULTROX unit as indicated by the TOC and COD analysis, an extensive organic characterization program will be conducted on the effluent from the test system at RMA. Several runs will be made using "best run" parameter values from which effluent samples and exhaust gas samples will be collected and analyzed. These results will be presented in the final report.

#### Metals Analysis

54. The results of the metals analysis performed on the samples from the ULTROX system indicated that the UV/ozone oxidation process had essentially no effect on the concentration of metals in the RMA groundwater. Since no variations in concentrations occurred, only metal analyses from the effluent samples have been included in this report. Table 4 presents a summary of the results of the metal analyses conducted on the effluent samples along with the recommended concentration limits.

55. The concentrations of the various metals remained fairly constant over the duration of the testing program. Only manganese and sodium

concentrations were found to be above the recommended level. Additional metal analyses are being conducted at WES and will be presented in the final report.

#### General Analysis

56. The results of the general analysis performed on the samples from the ULTROX system are given in Appendix D. A summary of these data is presented in Table 5.

57. The values associated with most of the parameters remained unchanged as a result of the UV/ozone oxidation process. These data indicate that most of the nitrite was oxidized to nitrate during the oxidation process. Also, ortho-phosphate concentrations increased as a result of the destruction of DIMP molecules. No other significant changes were indicated.

58. Two anions were found in concentrations that exceeded recommended levels. Chloride and sulfate concentrations averaged 450 mg/l and 700 mg/l, respectively, while the recommended limit for each is 250 mg/l.

#### Optimized Field Unit Operating Conditions

59. The optimized field unit operating conditions with estimated effluent DIMP concentrations and operating costs for a 10,000 gph treatment system are presented in Table 6. The operating conditions are grouped on the basis of a corresponding grouping of estimated DIMP effluent concentrations. These values were obtained from a computer-aided analysis of the information obtained from the test runs made on RMA groundwater. The effluent DIMP concentrations have not been verified but will be checked during a series of test runs that will be initiated 1 October 1977.

60. The estimated DIMP effluent concentrations range from 0 to 150 ppb. The estimated operating costs for each range of DIMP effluent concentration are as follows:

<u>DIMP Effluent Concentration, ppb</u>	<u>Operating Costs, \$/1000 gal</u>
0 - 2	0.70
9 - 11	0.67
48 - 50	0.64
73 - 74	0.60
99 - 101	0.57
148 - 149	0.54

There is a difference of \$0.16 per 1000 gal of water treated between the 150 ppb and the 0-2 ppb range in effluent concentration. The estimated operating costs cover the cost of power for ozone generation and UV light generation. Capital costs and maintenance costs will <sup>be</sup> calculated after verification of the optimized operational parameters and presented in the final report.

61. Additional information concerning the optimized operating conditions along with verification data from the additional test runs to be made at RMA will be included in the final report.

#### Work to be Completed in FY 78

62. This report presents all information completed to date on UV/ozone oxidation of RMA groundwater using the ULTROX unit. During the first quarter of FY 78, additional studies will be conducted at RMA in order to verify the information generated by the computer-assisted <sup>aided</sup> analysis of the data from the test runs. After this verification procedure is completed, the recommended operational parameters will be used to determine the design of a full size pilot plant. The evaluation of any system modification will be conducted through use of a bench-scale UV/ozone unit. All information obtained in the FY 78 work with the ULTROX unit will be presented in a final report.

## PART IV: CONCLUSIONS AND RECOMMENDATIONS

### Conclusions

63. The following conclusions are based on the data obtained from the limited study at RMA during the summer of 1977.

- a. The UV/ozone oxidation process can reduce the concentrations of organic contaminants found in RMA groundwater to low levels (DIMP <20 ppb and TOC <4 ppm).
- b. The percent disappearance of DIMP is extremely dependent on the ozone mass flow rate (up to a value of 300 mg/l) and on the number of UV lamps in operation (up to 10).
- c. Higher ozone mass flow rates and UV intensities are needed to effect a high TOC reduction than are needed to effect a fairly complete disappearance of DIMP.
- d. There are certain unidentified decomposition, organic contaminants (very low concentrations) that are not destroyed by the UV/ozone oxidation process.
- e. The UV/ozone oxidation process can effect the disappearance of DIMP for an operational cost of less than \$0.75 per 1000 gallons on the basis of a 10,000 gph system.
- f. Manganese, sodium, chloride, and sulfate concentrations in PW3 are above recommended levels. The concentrations of these contaminants are not affected by the UV/ozone process.

### Recommendations

64. Some additional information is needed to complete this study on the applicability of UV/ozone treatment to RMA groundwater. In order to obtain this information, the following efforts are recommended.

- a. Verification test runs should be conducted using the optimum operating conditions provided by the computer-aided analysis procedure. Samples of exhaust gas and effluent should be collected during these runs to be used in an extensive organics characterization study.
- b. An additional test program should be initiated in which the UV/ozone process is used to treat groundwater from other source wells located on RMA because of the need to assess the effect of the UV/ozone process on other contaminants not present in the groundwater used in this study.
- c. Additional data obtained from further test runs should be used to refine the model of the UV/ozone process being developed.

#### REFERENCES

1. Timofeeff, N. P., "Sampling Procedures and Contaminant Migration in Soils," paper presented in Seventh Annual Symposium on Environmental Research, Edgewood Arsenal, MD, 14-16 Sep 1976.
2. Carnahan, R. P., Lent, D., Annzzolin, R., and Rutherford, G., "Treatability Studies of Seep Water from the Bog at Rocky Mountain Arsenal," paper presented at Seventh Annual Symposium on Environmental Research, Edgewood Arsenal, MD, 14-16 Sep 1976.
3. Buhts, R. E., Malone, P. G., and Thompson, D. W., "Evaluation of Ultraviolet/Ozone Treatment of Rocky Mountain Arsenal (RMA) Groundwater (Treatability Study)," Draft Report, Mar 1977, U. S. Army Engineer Waterways Experiment Station, CE, Vicksburg, MS.
4. Calgon Corporation, "Removal of Trace Organics from Groundwater Using Granular Activated Carbon," 30 Mar 1977, Denver, CO.
5. American Public Health Association, et al, Standard Methods for the Examination of Water and Wastewater, 14th ed., American Public Health Association, Washington, D. C., 1975.
6. Procedures for Water and Wastewater Analysis, 2nd ed., HACH Chemical Company, Ames, Iowa, 1975.

Table 1  
General Analysis Conducted on RMA Groundwater

Parameter	Method
Alkalinity	Standard Methods
Chloride	Standard Methods
Conductivity	Conductivity Meter, YSI Model 31
Dissolved Oxygen	Standard Methods
Fluoride	HACH - Spectronic 20
Nitrate	HACH - Spectronic 20
Nitrite	HACH - Spectronic 20
pH	pH Meter, Orion Model 399A
Phosphate (Ortho)	HACH - Spectronic 20
Sulfate	HACH - Spectronic 20
Solids	Standard Methods

Table 2  
Operational Parameters for Various UV/Ozone Test Runs

Test Run No.	Influent Flow l/min	No. Lamps Operating	Ozone			Gas Flow l/min	Oxygen	
			Mass Flow* mg/min	Input Fraction %	Exhaust Gas Mass Flow mg/min		Influent mg/l	Dissolved Effluent mg/l
1	3.0	1-30 odd	534	1.3	--	27.0	--	--
2	2.7	1-30 odd	702	1.8	67.5	27.0	--	--
3	2.4	1-30 odd	680	1.7	--	27.0	--	--
4	3.0	All	583	1.5	114.	27.0	--	--
5	3.0	None	600	1.5	173.	27.0	--	--
6	2.4	All	600	1.5	--	27.0	7.7	33.6
7	2.4	1-15 odd	600	1.5	62.1	27.0	6.8	37.4
8	3.0	None	400	1.0	162.	27.0	5.7	38.5
9	2.4	All	504	1.3	97.0	27.0	5.7	38.5
10	2.5	All	300	1.8	12.7	11.5	7.0	38.3
11	3.0	All	200	1.8	4.2	8.0	6.8	35.7
12	3.0	16-30 even	390	1.0	110.	27.0	7.3	43.8
13	2.4	16-30 even	567	1.5	137.	27.0	6.3	43.3
14	2.4	7-25 odd	486	1.3	67.0	27.0	7.0	37.6
15	2.4	16-30 All	500	1.8	96.0	19.0	5.4	41.4
16	3.0	1-15 odd	390	1.6	40.8	17.0	5.2	46.0
17	2.7	17-29 odd	600	1.8	110.	23.3	7.1	47.3
18	2.0	7-19 odd	302	1.0	74.0	21.0	6.8	40.5
19	2.0	16-30 even	202	1.0	37.7	14.0	7.1	41.4
20	2.1	1-30 odd	251	1.2	17.5	14.6	6.8	39.2
21	2.2	None	203	1.7	50.2	8.2	7.1	43.8
22	3.5	All	587	1.8	72.5	23.3	7.5	40.4
23	3.1	16-30 even	406	1.6	58.8	17.5	7.7	43.7
24	2.4	All	594	1.5	87.0	28.0	7.0	39.2
25	2.4	None	606	1.8	104.	23.3	7.0	48.2

(Continued)

\* Ozone flow split between stages for Runs 27 through 35.

Table 2 (Concluded)

Test Run No.	Influent Flow l/min	No. Lamps Operating	Ozone			Dissolved in Effluent			Oxygen		
			Mass Flow* mg/min	Fraction %	Mass Flow mg/min	Fraction %	mg/min	l/min	Influent mg/l	Dissolved Effluent mg/l	Gas Flow l/min
26	2.2	16-30 even	606	1.8	77.2	0.23	8.7	23.3	7.1	44.5	
27	2.4	All	200 200 100	1.5	72.0	0.22	1.8	23.3	6.3	30.1	
28	2.0	7-19 odd	106 77 77	1.0	60.0	0.23	2.9	18.5	6.3	33.3	
29	2.1	1-30 odd	78 64 43	1.2	14.2	0.09	1.5	10.8	6.2	31.6	
30	3.0	All	200 100 100	1.5	38.5	0.15	1.4	18.5	6.6	25.8	
31	2.2	16-30 even	201 152 100	1.8	--	--	6.9	17.7	6.5	30.9	
32	2.4	All	206 103 52	1.5	43.7	0.18	None	16.7	7.0	28.7	
33	2.0	7-19 odd	108 54 54	1.0	48.5	0.23	1.7	15.0	6.7	32.8	
34	2.4	20-30 even	165 124 41	1.4	75.1	0.31	5.2	16.5	7.0	32.7	
35	3.0	19-29 odd	194 196 98	1.6	138.	0.45	10.8	21.5	7.2	34.8	
61	4.0	1-30 odd	330	2.3	45.4	0.32	17.8	10.0	7.1	32.2	
62	3.0	1-30 odd	330	2.3	55.7	0.39	13.2	10.0	7.2	31.4	
63	2.0	1-30 odd	330	2.3	21.2	0.15	16.5	10.0	7.1	30.0	
64	1.0	1-30 odd	330	2.3	41.5	0.29	39.4	10.0	7.9	26.9	
71	4.0	1-30 All	350	2.5	32.1	0.23	8.6	10.0	8.1	31.3	
81	4.0	1-30 odd	602	2.1	119.	0.42	9.4	20.0	7.4	32.7	
82	4.0	1-30 odd	412	1.4	66.8	0.23	7.2	20.0	7.1	31.3	
83	4.0	1-30 odd	226	0.8	36.0	0.13	5.2	20.0	7.2	31.2	
84	4.0	1-30 odd	0	0	0	0	0	20.0	7.0	31.0	
91	4.0	1-30 odd	527	3.7	45.0	0.32	1.2	10.0	6.3	32.9	
92	4.0	1-30 odd	344	2.4	26.6	0.19	4.5	10.0	6.3	32.3	
93	4.0	1-30 odd	40	0.3	6.2	0.04	7.1	10.0	6.6	31.0	
94	4.0	1-30 odd	0	0	0	0	0	10.0	6.6	30.5	
95	4.0	1-30 odd	0	0	0	0	0	0	--	--	

\* Ozone flow split between stages for Runs 27 through 35.

Table 3  
Organic Analysis for Various UV/Ozone Test Runs

Test Run No.	DMP				TOC				COD		
	Midstream		Effluent		Midstream		Effluent		Influent Conc. mg/l	Effluent Conc. mg/l	Reduction %
	Influent Conc. ppb	Concentration ppb	Disappearance %	Concentration ppb	Influent Conc. ppm	Concentration ppm	Reduction %	Concentration ppm			
1	2793	---	---	51.7	---	4.7	---	3.1	---	---	---
2	2709	152.	94.4	23.1	99.2	9.3	---	4.0	---	---	---
3	2906	141.	95.1	25.0	99.1	9.7	---	3.0	---	---	---
4	2910	137.	95.3	22.0	99.2	8.9	59.6	2.8	---	---	---
5	2965	1134	61.8	739.	75.1	10.1	46.3	5.8	---	---	---
6	2936	103.	96.5	14.6	99.5	9.6	60.4	3.0	---	---	---
7	2820	336.	88.1	48.0	98.3	8.6	53.5	2.9	---	---	---
8	2792	1582	43.0	1215	56.5	7.6	21.1	5.6	---	---	---
9	2659	178.	93.3	46.0	98.3	7.2	50.0	3.2	---	---	---
10	2835	361.	87.3	78.0	97.3	9.4	51.1	3.3	---	---	---
11	2791	822.	70.6	298.	89.3	8.4	41.7	7.7	---	---	---
12	2780	469.	83.1	381.	86.3	7.9	39.2	5.4	---	---	---
13	2993	183.	93.9	87.0	97.1	8.6	47.7	3.9	18.7	4.4	76.5
14	2870	170.	94.1	39.0	98.6	7.1	53.5	3.3	18.7	4.6	75.4
15	2549	150.	94.1	69.0	97.3	7.5	46.7	4.2	20.6	14.6	29.1
16	2447	618.	74.7	95.0	96.1	8.3	30.1	4.8	19.3	10.4	46.1
17	2421	188.	92.2	99.0	95.9	8.9	50.6	3.9	17.5	8.6	50.9
18	3293	390.	88.2	91.0	97.2	12.1	68.6	3.6	16.5	6.8	58.8
19	2762	2047	25.9	1633	40.9	7.7	42.9	4.5	18.3	8.9	51.4
20	2551	177.	93.1	38.0	98.5	7.8	53.8	3.8	20.4	5.0	75.5
21	2966	981.	66.9	513.	82.7	7.7	26.0	5.2	18.1	7.9	56.4
22	2558	74.8	97.1	6.0	99.8	9.4	58.5	2.3	15.1	2.9	80.8
23	2721	185.	93.2	100.	96.3	8.1	39.5	4.9	20.8	10.6	49.0
24	2820	48.0	98.3	3.8	99.9	7.8	64.1	2.1	17.6	1.6	90.9
25	2916	532.	81.8	260.	91.1	7.7	16.9	6.0	18.0	8.4	53.3

(Continued)

Table 3 (Concluded)

Test Run No.	DIMP				TOC				COD			
	Midstream		Effluent		Midstream		Effluent		Influent		Effluent	
	Influent Conc. ppb	Concentration ppb	Disappearance %	Concentration ppb	Influent Conc. ppm	Concentration ppm	Reduction %	Concentration ppm	Influent Conc. mg/l	Effluent Conc. mg/l	Reduction %	Concentration ppm
26	3062	53.8	98.2	23.4	9.6	4.7	51.0	4.1	19.2	8.2	57.3	57.3
27	3086	41.4	98.7	13.0	9.7	3.6	62.9	3.4	18.9	6.2	67.2	67.2
28	2070	255.	87.7	79.0	9.8	4.9	50.0	4.1	22.1	9.1	58.2	58.8
29	2551	165.	93.5	87.0	8.7	5.0	42.5	4.4	25.2	9.3	63.1	63.1
30	2572	65.0	97.5	11.8	9.7	4.0	58.8	3.0	19.2	3.3	82.8	82.8
31	2316	56.0	97.6	31.4	8.6	4.4	48.8	4.0	13.7	9.5	30.7	30.7
32	2804	64.0	97.7	26.0	8.2	3.5	57.3	2.9	20.4	5.1	75.0	75.0
33	3201	502.	84.3	210.	8.0	4.8	40.0	4.5	20.3	10.3	49.3	49.3
34	2785	157.	94.4	158.	7.1	4.1	42.3	4.3	22.2	10.9	50.9	50.9
35	2516	102.	95.9	78.0	7.9	1.6	79.7	4.2	21.8	9.9	54.6	54.6
61	3440	209.	93.9	36.3	--	--	--	--	--	--	--	--
62	2406	125.	94.8	17.9	--	--	--	--	--	--	--	--
63	3201	73.8	97.7	7.3	--	--	--	--	--	--	--	--
64	2952	27.2	99.1	3.2	--	--	--	--	--	--	--	--
71	2939	67.0	97.7	7.0	--	--	--	--	--	--	--	--
81	2523	96.9	96.2	9.8	--	--	--	--	--	--	--	--
82	3340	316.	90.5	55.8	--	--	--	--	--	--	--	--
83	4106	911.	77.8	200.	--	--	--	--	--	--	--	--
84	4106	3957	3.6	1985	--	--	--	--	--	--	--	--
91	2271	86.5	96.2	11.4	--	--	--	--	--	--	--	--
92	2309	205.	91.1	46.0	--	--	--	--	--	--	--	--
93	2697	2002	25.8	1498	--	--	--	--	--	--	--	--
94	3326	3144	5.5	2515	--	--	--	--	--	--	--	--
95	2843	2879	--	2661	--	--	--	--	--	--	--	--

Table 4  
Summary of Analysis - Metals

<u>Metal</u>	<u>Limit*</u> <u>mg/l</u>	<u>Effluent</u>			
		<u>Mean</u> <u>mg/l</u>	<u>Std Dev</u> <u>mg/l</u>	<u>Max</u> <u>mg/l</u>	<u>Min</u> <u>mg/l</u>
Beryllium	0.1	<0.005	--	--	--
Boron	0.75	0.66	0.02	0.72	0.60
Cadmium	0.01	<0.005	--	--	--
Calcium	--	105	12	113	68
Chromium	0.05	<0.01	--	--	--
Copper	1.0	<0.1	--	--	--
Iron	0.3	<0.1	--	--	--
Magnesium	125	63.7	3.2	68.6	58.2
Manganese	0.05	.11	.02	.13	.10
Potassium	--	5.76	.22	6.05	5.56
Sodium	250	867	25	910	850
Zinc	5.0	<0.1	--	--	--

\* Quality Criteria for Water, U. S. Environmental Protection Agency,  
 Washington, D. C., 1976.

Table 5  
Summary of Analysis - General

Parameter	Influent			Midstream			Effluent		
	Mean	Std Dev	Max	Mean	Std Dev	Max	Mean	Std Dev	Max
Alkalinity, mg/l	322	34	408	323	33	409	322	33	400
Chloride, mg/l	451	21	529	451	19	513	447	18	502
Conductivity, $\times 10^3$ $\mu$ mhos/cm	2.80	0.2	3.30	2.80	0.2	3.25	2.80	0.3	3.75
Fluoride, mg/l	1.60	0.13	1.98	1.60	0.15	2.00	1.60	0.14	1.98
Nitrate, mg/l	1.1	0.6	3.5	1.3	0.5	2.0	1.4	0.6	2.6
Nitrite, $\mu$ g/l	97	81	296	8	3	16	7	2	14
pH	8.2	0.3	8.6	8.3	0.2	8.8	8.4	0.1	8.8
Phosphate (Ortho), mg/l	0.49	.10	.69	.65	.14	.87	.77	.17	.95
Sulfate, mg/l	704	101	873	700	104	868	709	113	868
Temperature, °C	21.2	1.7	26.0	18.0	--	--	23.2	1.9	27.0
Total Solids, mg/l	2005	74	2157	1856	--	--	2052	86	2204
Total Dissolved Solids, mg/l	1991	96	2193	1926	--	--	2047	67	2146

Table 6  
Optimized Field Unit Operating Conditions

Influent Flow g/min	Ozone Mass Flow			Number of Lamps			Estimated DIMP Effluent Concentration ppb	Estimated Operating Costs \$/1000 gal
	Sect 1 mg/min	Sect 2 mg/min	Sect 3 mg/min	Total mg/min	Sect 1	Sect 2	Sect 3	
3.0	176	132	92	400	0	5	5	0.70
3.0	342	174	84	600	5	3	0	0.73
3.0	160	80	400	600	0	5	5	0.70
3.0	200	200	100	500	0	3	5	0.67
3.0	300	150	150	600	0	3	5	0.73
3.0	285	145	70	500	0	3	5	0.67
3.0	200	200	100	500	0	3	5	0.67
3.0	250	190	60	500	0	3	5	0.67
3.0	200	200	100	500	5	3	0	0.67
3.0	220	165	115	500	0	3	5	0.67
3.0	200	200	100	500	0	3	5	0.67
3.0	150	114	36	300	0	5	5	0.64
3.0	171	87	42	300	0	5	5	0.64
3.0	150	114	36	300	0	5	5	0.64
3.0	200	152	48	400	0	3	5	0.60
3.0	228	116	56	400	0	3	5	0.60
3.0	200	152	48	400	5	3	0	0.60
3.0	80	80	40	200	0	5	5	0.57
3.0	100	76	24	200	0	5	5	0.57
3.0	114	58	28	200	0	5	5	0.57
3.0	171	87	42	300	5	3	0	0.54
3.0	150	114	36	300	5	3	0	0.54

## APPENDIX A: OPERATIONAL PROCEDURES

### FOR THE ULTROX SYSTEM

#### Start-up Procedure

1. The following procedure was used to start-up the ULTROX system:
  - a. Check the pressure gage associated with the oxygen cylinder supplying oxygen to the ozone generator to assure that sufficient oxygen is available.
  - b. Set the UV lamp pattern. This is done by disconnecting the upper lamp contact plug from the lamps which are not to be used. Turn on the lamp switch and check the LED display to assure that the lighting sequence is correct.
  - c. Plug in the catalytic decomposition chamber for the effluent gas.
  - d. Turn on the cooling water to the ozone generator and adjust its flow to at least 1 to 2 liters per minute.
  - e. Calculate the necessary oxygen pressure and flow rate for the given ozone concentration and mass flow as described in Appendix C of this report.
  - f. Open the valve on each oxygen cylinder and adjust the pressure regulator to approximately 5 psig above the pressure calculated in step e above.
  - g. Check that the rheostat on the ozone generator is set on zero and then turn on the main power switch.
  - h. Adjust the oxygen pressure and flow rate to the values calculated in step e above.
  - i. Adjust the rheostat on the ozone generator to a low setting to start the generation of ozone.
  - j. Adjust the gas flowmeters on the ULTROX unit to the desired flow rates. Check the oxygen pressure and flow rate to assure that they have not changed.
  - k. Open the liquid feed line valve and turn on the water pump. Adjust the pump to the desired flow rate using the flowmeter in the feed line.
  - l. Check the ozone concentration as described in Appendix B of this report. Adjust the rheostat setting on the ozone generator as necessary. Also adjust the oxygen pressure and flow rate if needed.

- m. Check the liquid flow rate at the effluent stream and adjust the water pump as necessary.
- n. Repeat steps l and m every 5 minutes until the desired settings (values) are obtained and then at 30 minute intervals through the test run.

#### Shut-down Procedure

2. The following procedure was used to shut-down the ULTROX unit after completion of a run:

- a. Turn off the liquid pump and close the feed line valve.
- b. Slowly turn the rheostat on the ozone generator to zero. Allow several minutes of oxygen flow through the generator to flush any residual ozone from the generator.
- c. Turn off the valves on the oxygen cylinders and allow the pressure in the regulator to drop to zero.
- d. Close the regulator valve and shut off the power to the ozone generator.
- e. Turn off the cooling water to the generator.
- f. Turn off the UV lamps in the ULTROX unit.
- g. Shut off the power to the catalytic decomposition chamber.

APPENDIX B: OZONE SAMPLING AND  
ANALYSIS PROCEDURES

Sampling

Input Gas

1. The ozone sampling procedure used on the input gas was suggested by the ozone generator manufacturer. A breaker was filled with a 2.5 percent by weight (%/wt) potassium iodide solution. The ozone flow from a tee in the ozone discharge line was adjusted to obtain a reading of 10 scale units on the sample flowmeter (Figure B1). When the flowmeter indicated a steady flow, the sampling tube was immersed in the beaker of potassium iodide solution and allowed to remain for 30 seconds. The sampling tube was then removed and the valve controlling the ozone flow through the sampling tube was closed. The sample was acidified with a .1 M solution of sulfuric acid and analyzed.

Exhaust Gas

2. The ozone in the exhaust gas was sampled at the liquid-gas separator on the ULTROX unit. The exhaust gas pressure was only slightly above atmospheric, therefore a vacuum pump was used to pull a sample of gas through a gas washing bottle containing a 2.5 %/wt potassium iodide solution. The pump control valve was set to 1 l/min and allowed to run for 1 minute. The vacuum pump was then stopped and the sample from the gas washing bottle was acidified with a .1 M solution of sulfuric acid and analyzed.

Dissolved in the Effluent

3. The dissolved ozone contained in the effluent from the ULTROX system was determined as follows. A 100 ml sample of effluent was obtained and immediately poured into a flask containing 2.5 grams of potassium iodide. The sample was mixed until the potassium iodide disappeared. Then the sample was acidified with a .1 M solution of sulfuric acid and analyzed.

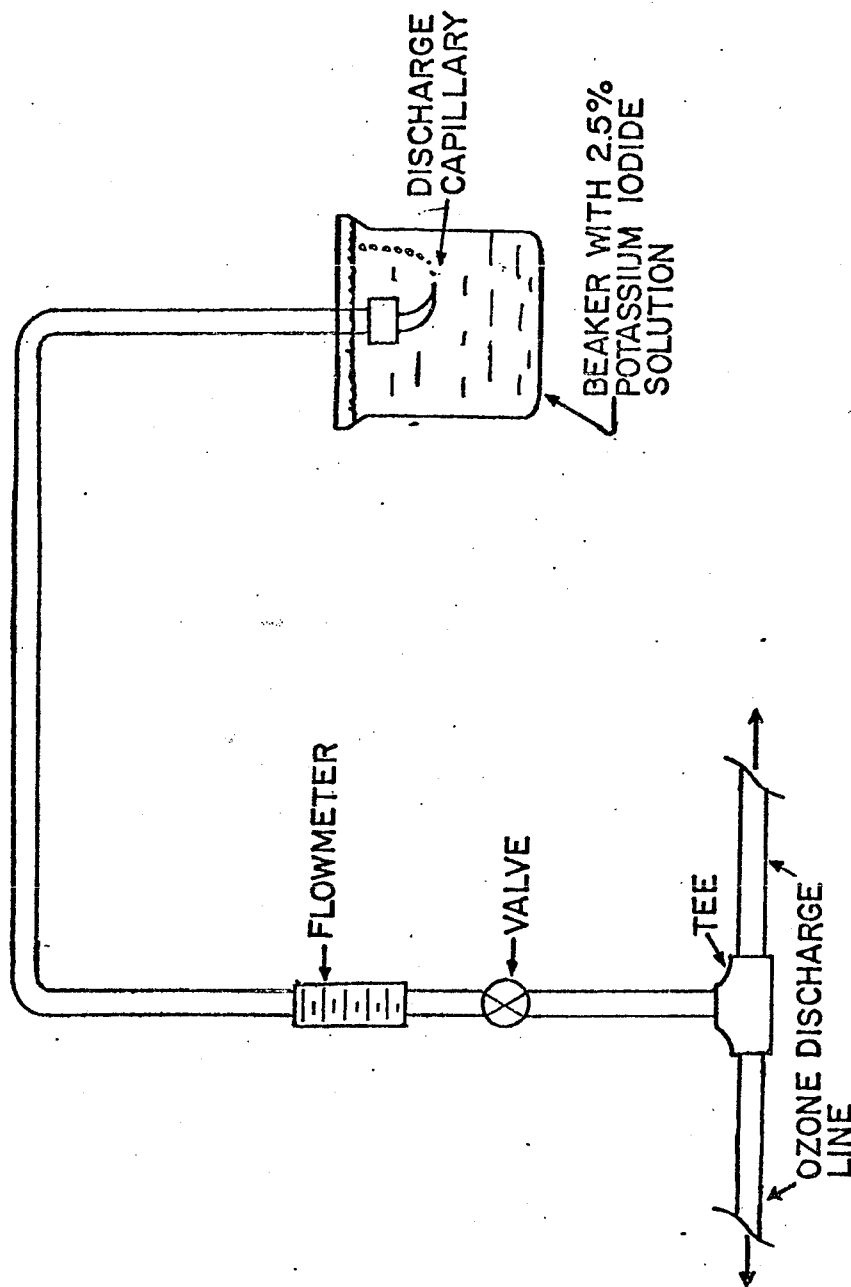


Figure B1. Ozone measurement set-up

### Analysis

4. The acidified samples were transferred to a glass beaker on a magnetic stirrer. A titration was performed using a .1 N solution of sodium thiosulfate as a titrant and a 1 %/wt starch solution as an indicator. The percent by weight of ozone in the gas stream was calculated using the following equations:

$$\text{Wt } O_3 \text{ (mg/l)} = \frac{(\text{ml}) \times (\text{N}) \times (24)}{(.124)} \quad (1)$$

$$\text{Wt \% } O_3 = \frac{(\text{Wt } O_3) \times (100) \times (T)}{(1429) \times (273.16)} \quad (2)$$

where: ml = mililiters of titrant used

N = normality of titrant

T = temperature, °K

5. The ozone mass flow rate was determined by the following equation:

$$O_3 \text{ Mass Flow Rate (mg/min)} = \text{Wt } O_3 \text{ (mg/l)} \times O_2 \text{ Flow (l/min)} \quad (3)$$

APPENDIX C: DETERMINATION OF OPERATIONAL  
PARAMETERS FOR THE ULTROX SYSTEM

Oxygen Flow Rate

1. The oxygen flow rate to the OREC ozone generator is determined as follows. For a particular pressure setting on the oxygen regulator and a particular tube scale reading on the flowmeter, the flowmeter graph (Figure C1) indicates the resulting oxygen flow to the generator. The flow rate is given in  $\text{ft}^3/\text{min}$  and must be converted to  $\ell/\text{min}$  as follows:

$$\text{O}_2 \text{ flow (ft}^3/\text{min)} \times 28.32 = \text{O}_2 \text{ flow (}\ell/\text{min)} \quad (1)$$

Ozone Flow Rate

2. For a given flow rate, the ozone production graph (Figure C2) can be used to determine the amperage setting required for any desired ozone flow given in  $\text{mg}/\ell$ . The ozone mass flow rate can then be determined as follows:

$$\text{O}_3 \text{ Mass flow rate (mg/min)} = \text{Wt/O}_3 \text{ (mg/}\ell\text{)} \times \text{O}_2 \text{ flow (}\ell/\text{min)} \quad (2)$$

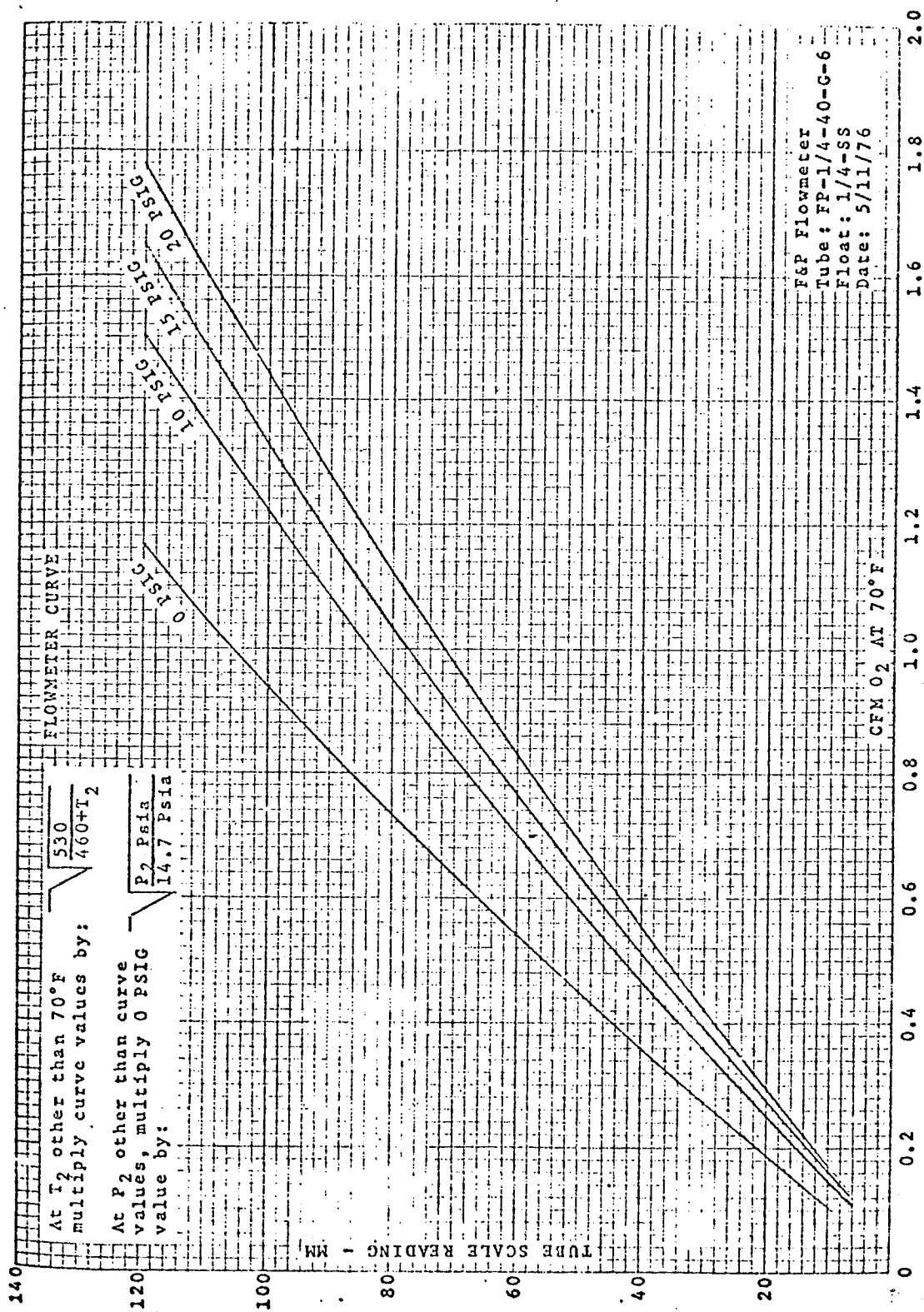


Figure C1. Flowmeter curve for OREG model 03B20 ozone generator

# OZONE PRODUCTION CHART

OZONATOR  
03B-0 Series  
5/20/74

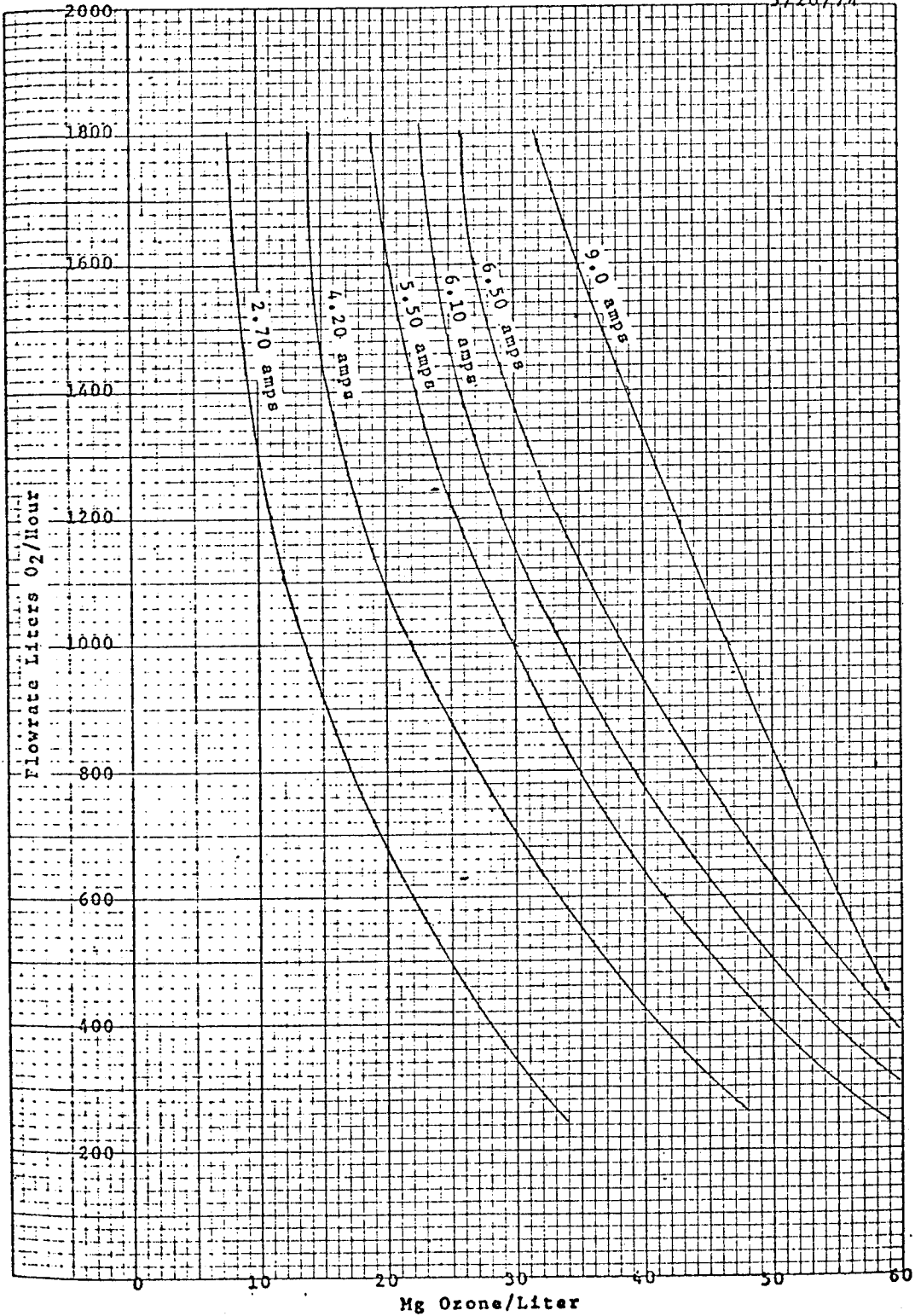


Figure C2. Ozone production chart for OREC model 03B20 ozone generator

APPENDIX D; GENERAL ANALYSIS FROM  
VARIOUS UV/OZONE TEST RUNS

1. Table D1 contains the results of general analyses performed on samples from various UV/ozone test runs using RMA groundwater. These data were used to develop the Summary of Analysis - General presented as Table 5 in this report.

Table D1  
General Analysis for Various UV/Ozone Test Runs

Test Run No.	Alkalinity			Chloride			Conductivity			Fluoride			Nitrate			Nitrite		
	Inf	Mid	Eff	Inf	Mid	Eff	Inf	Mid	Eff	Inf	Mid	Eff	Inf	Mid	Eff	Inf	Mid	Eff
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	µmhos/cm ×10 <sup>3</sup>	µmhos/cm ×10 <sup>3</sup>	µmhos/cm ×10 <sup>3</sup>	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L
1	--	346	344	--	--	--	2.80	2.95	2.68	--	1.49	1.53	--	1.1	1.4	--	9	11
2	348	344	346	--	464	470	2.95	2.80	2.82	1.46	1.43	1.40	1.1	2.0	1.5	13	9	9
3	--	348	346	--	--	--	2.70	2.70	2.75	1.51	1.49	1.49	1.4	1.4	1.1	263	9	7
4	310	322	324	470	462	459	3.00	3.10	3.10	--	1.47	1.47	3.5	2.3	2.6	280	4	8
5	336	344	346	475	470	448	3.30	3.10	3.15	1.60	1.60	1.55	0.8	0.6	0.2	22	8	7
6	346	346	338	464	464	464	2.80	2.80	2.80	1.60	1.64	1.62	0.8	1.7	1.4	30	10	7
7	354	350	354	459	459	462	3.30	3.25	3.75	1.51	1.51	1.52	1.1	0.6	1.0	26	16	8
8	342	338	342	462	451	456	2.80	2.82	2.70	1.52	1.43	1.40	0.6	0.8	0.8	24	4	5
9	334	350	354	454	448	437	3.30	3.25	3.75	1.51	1.51	1.52	1.1	0.6	1.0	26	16	8
10	336	338	336	459	464	459	3.15	3.15	3.15	1.53	1.53	1.52	1.1	1.6	1.7	174	14	14
11	342	342	344	475	486	459	3.30	3.20	3.10	1.55	1.58	1.55	2.0	1.7	2.0	296	9	11
12	344	344	342	443	437	443	2.90	2.90	2.85	1.58	1.55	1.58	1.1	1.5	1.4	82	8	5
13	342	344	338	443	448	448	--	--	--	1.73	1.73	1.71	1.5	2.0	2.2	210	8	6
14	342	342	338	448	443	448	2.60	2.60	2.60	1.73	1.83	1.71	1.1	1.7	1.7	139	9	8
15	338	336	336	437	437	432	2.65	2.75	2.70	1.71	1.71	1.76	0.9	1.7	1.6	135	6	6
16	408	409	400	408	409	400	2.50	2.45	2.50	1.98	1.98	1.98	1.4	1.1	0.6	87	11	9
17	316	318	314	432	421	416	2.50	2.50	2.50	1.91	2.00	1.93	1.1	1.3	1.7	131	7	4
18	294	294	304	437	437	432	2.95	2.90	2.90	1.67	1.69	1.65	1.1	1.6	1.7	48	6	4
19	296	298	288	437	437	443	2.80	2.85	2.85	1.65	1.69	1.67	1.7	1.9	2.2	63	9	9
20	298	298	294	443	432	437	3.10	2.80	2.65	1.69	1.72	1.69	1.1	1.4	1.4	91	4	2
21	302	298	298	432	437	432	2.70	2.70	2.70	1.63	1.68	1.71	1.1	1.4	2.3	79	6	6
22	288	280	280	529	513	502	2.80	2.80	2.82	1.75	1.73	1.71	0.8	1.7	1.7	59	8	6
23	284	286	288	443	437	448	2.80	2.85	2.80	1.75	1.75	1.75	0.8	0.8	0.8	66	8	6
24	276	276	284	448	446	429	2.82	2.80	2.82	1.65	1.73	1.71	0.8	0.8	1.1	56	8	6
25	280	273	272	443	448	448	2.76	2.75	2.80	1.69	1.69	1.71	0.8	0.8	0.8	56	8	8
26	272	275	269	448	446	451	2.70	2.80	2.80	--	--	--	0.6	0.6	0.6	61	8	8
27	--	--	--	451	448	437	2.78	2.80	2.80	--	--	--	0.4	0.4	0.6	46	4	6
28	276	274	274	446	456	451	2.70	2.65	2.70	--	--	--	--	--	--	66	2	9
29	--	--	--	451	459	454	2.60	2.60	2.60	--	--	--	--	--	--	--	--	--
30	--	--	--	448	448	448	2.65	2.65	2.65	--	--	--	--	--	--	--	--	--
31	--	--	--	454	459	456	2.70	2.65	2.65	--	--	--	--	--	--	--	--	--
32	--	--	--	--	--	--	2.70	2.65	2.65	--	--	--	--	--	--	--	--	--
33	--	--	--	--	--	--	2.65	2.70	2.70	--	--	--	--	--	--	--	--	--
34	--	--	--	--	--	--	2.60	2.60	2.60	--	--	--	--	--	--	--	--	--
35	--	--	--	--	--	--	2.60	2.60	2.55	--	--	--	--	--	--	--	--	--

(Continued)

Table D1 (Concluded)

Test Run No.	pH		Phosphate (Ortho)			Sulfate		Temperature		Total Solids		Total Dissolved Solids	
	Inf	Mid	Inf	Mid	Eff	Inf	Mid	Inf	Eff	Inf	Eff	Inf	Eff
			mg/l	mg/l	mg/l	mg/l	mg/l	°C	°C	mg/l	mg/l	mg/l	mg/l
1	---	8.8	---	---	---	---	757	---	---	---	---	---	---
2	7.6	7.7	---	---	---	710	730	18.0	22.2	---	---	---	---
3	8.6	8.6	---	---	---	745	723	18.0	22.2	---	---	---	---
4	7.3	8.4	0.69	0.75	0.94	705	708	22.0	26.0	---	---	---	---
5	8.0	8.4	---	0.46	0.45	745	665	22.0	22.0	2157	2148	2193	2112
6	8.1	8.7	0.38	0.77	0.92	730	650	21.0	25.0	---	---	---	---
7	8.1	8.3	0.55	0.71	0.89	710	710	25.0	26.0	---	---	---	---
8	7.9	8.2	0.55	0.58	0.89	665	710	21.5	21.5	1912	2024	2008	2118
9	8.1	8.3	0.63	0.80	0.89	710	710	22.0	26.0	---	---	---	---
10	8.2	8.1	0.46	0.63	0.95	758	738	22.0	26.0	2038	2130	2008	2100
11	8.1	8.0	0.46	0.51	0.61	757	757	24.0	26.0	2016	2159	2102	2146
12	7.8	8.4	0.43	0.46	0.65	682	682	21.5	22.5	---	---	---	---
13	8.0	8.2	0.46	0.82	0.87	730	758	24.0	26.0	1991	1900	1972	2086
14	8.1	8.5	0.55	0.87	0.95	443	454	26.0	27.0	---	---	---	---
15	8.1	8.4	0.50	0.83	0.89	758	738	24.0	26.0	---	---	---	---
16	8.0	8.2	0.46	0.53	0.71	633	682	21.0	22.5	---	---	---	---
17	8.2	8.2	0.52	0.67	0.75	710	710	22.0	22.0	1856	1951	1824	1926
18	7.9	8.1	0.59	0.72	0.74	668	745	24.0	25.0	---	---	---	---
19	8.0	8.2	0.31	0.50	0.52	750	768	23.0	23.0	1986	2034	1926	1954
20	8.4	8.4	0.34	0.59	0.74	873	810	21.7	24.4	---	---	---	---
21	8.3	8.3	0.53	0.42	0.48	812	786	22.3	22.6	---	---	---	---
22	8.1	8.0	---	---	---	840	868	21.2	24.5	1955	1900	1879	2006
23	8.2	8.3	---	---	---	757	778	22.3	23.1	1984	2070	1930	2036
24	8.1	8.4	---	---	---	795	750	21.0	25.1	---	---	---	---
25	8.3	8.4	---	---	---	455	455	20.7	20.8	---	---	---	---
26	8.3	8.4	---	---	---	590	440	21.7	22.3	1987	2106	1932	1982
27	8.3	8.5	---	---	---	572	605	19.0	24.4	---	---	---	---
28	8.6	8.4	---	---	---	---	---	19.5	21.0	---	---	---	---
29	8.4	8.2	---	---	---	---	---	19.0	21.2	2020	2078	1954	2014
30	8.4	8.3	---	---	---	---	---	21.0	24.4	---	---	---	---
31	8.4	8.4	---	---	---	---	---	21.2	22.9	2110	2140	2038	2010
32	8.4	8.4	---	---	---	---	---	22.1	26.1	---	---	---	---
33	8.3	8.4	---	---	---	---	---	20.2	22.0	2030	2044	2078	2102
34	8.3	8.4	---	---	---	---	---	20.9	21.6	---	---	---	---
35	8.4	8.3	---	---	---	---	---	19.7	20.4	2032	2044	2032	2070